Imprinting Gd-based Metallic Glass and Its Application for Neutron Grating Interferometer

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学 位 論 文 題 目　Imprinting Gd-based Metallic Glass and its Application for Neutron Grating Interferometer（Gd 系金属ガラス転写法とその中性子干渉計用回折格子への応用
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論文内容要約

Problem and objective of the study

The absence of the long range atomic order and also the lack of crystalline defects such as dislocations and grain boundaries in metallic glasses make their behavior and properties noticeably different from those of crystalline alloys. Bulk metallic glasses show excellent mechanical, electrical, magnetic and chemical properties which are favorable for applications as engineering materials. Metallic glasses also exhibited viscous flow behavior at the supercooled liquid (SCL) state; which is between the glass transition temperature (T_g) and crystallization temperature (T_x). Viscosity drops drastically with the increase in temperature in the SCL region; and so, they are considered as a candidate material for micro/nano-forming by secondary working in the SCL region. However, the viscous workability varies depending on the thermal stability and viscosity of MG alloy system and composition in the SCL region. Indeed, despite viscous workability of MGs which is known as their unique characteristics, only a few of them can be deformed by viscous flow. To date there are many reports of patterning fragile and high thermally stable MG such as Pd-, Zr-, Pt- and Au-based MGs which show high viscous workability as lower viscosity and longer processing time are available for thermoplastic forming; however, processing of the metallic glass with less viscous workability has not well established in detail. Having taken into account the aforementioned, the present study intends to demonstrate high aspect ratio imprinting of Gd-based metallic glasses, as a model alloy with less viscous workability which is expected to be applied for neutron phase imaging.

Neutron radiography and tomography has proved itself as a method for non-destructive testing (NDT) of materials in the last years to reveal the inner part of many bulk magnetic materials as well as to obtain visual information on the microstructure of a given object. Neutrons interact with the atomic nucleus of the materials; so, they are able to show strong contrast between elements which are close to each other in the periodic table and also between two isotopes. Neutron differential phase contrast images is alternative method to conventional neutron absorption imaging and it is based on Talbot (-Lau) interferometer. This method has much more advantages compared to the conventional neutron absorption imaging, as a result of the fact that the phase sensitivity is much higher than the absorption contrast. In contrast to the conventional absorption imaging, where the contrast differences arise from the different attenuation properties of the materials, in the case of differential phase contrast imaging the image information originates from the wavelength change within the material. The principle of Talbot -Lau interferometry is based on Talbot effect or a self-imaging phenomenon by a transmission grating. A Talbot -Lau interferometer consists of three diffraction gratings; a source grating G0 to create individual line source, a phase grating G1 as a beam splitter and an analyzer grating G2 for phase stepping scan method. As the Gd absorbs neutrons so effectively, it can be used as G0 and G2 (G1 is usually made of Si). First Talbot interferometry for neutron imaging was established by F. Pfeiffer et al. in 2006.

Manufacturing of the analyzer grating G2 is the most challenging micro fabrication tasks, as it has the smallest period and it needs sufficient height to absorb neutrons. There are several approaches to fabricate grating for X-ray phase imaging made of Pd-based metallic glasses. To our knowledge; however, the manufacturing of the analyzer grating applied for neutron imaging made of metallic glasses is not well established. In the present research the Gd-based gratings for neutron grating interferometer were fabricated by imprinting method as imprinting promises low-cost, simple and time saving fabrication process of large area and high aspect ratio gratings. The difficulties of imprinting Gd-based MGs arise from their higher viscosity and the lower thermal stability with compared to the low viscosity of Pd-, Pt-, Au- and Zr- based MGs. We have accomplished a method to fabricate high aspect ratio diffraction grating made of Gd-based alloys which can be applied for neutron phase imaging based on grating interferometer. The specific objectives of this study are; 1) find best Gd-based metallic glass composition to fabricate as grating, 2) find optimum condition for imprinting to prepare high aspect ratio grating, and 3) perform neutron imaging using Gd-based alloy grating **(Chapter 1).**

Methodology and results of the study

The first challenge to fabricate Gd based metallic glass grating is to choose suitable Gd-based MG composition. To fabricate gratings which can interact with neutron effectively and show a high contrast image; in other words, have a better diffraction efficiency, the amount of Gd is better to be as high as possible; besides, the viscosity in SCLR should be low to allow the melt to flow easily into the grating mold, so the filling depth will be higher which is one of the important factors to have a high contrast image. Another consideration is thermal stability which should be high in order to have enough time to process before crystallization. Hence, several Gd-based metallic glasses ribbons in Gd-Co-Al, Gd-Ni-Al and Gd-Cu-Al (B) systems were prepared by melt spinning method and they were evaluated by thermal stability analysis, viscosity measurement and correlate them with formability judgment to select the best composition for fabrication as grating. The thermal stability of Gd-(Co, Ni, Cu)-Al (B) metallic glasses upon isothermal annealing between T_g and T_x have been investigated by DSC scans and measuring the incubation time which is the time of onset crystallization. Viscosity was investigated by TMA analysis, the Newtonian viscosity and its dependence on temperature is one of the most important factors to characterize the atomic mobility of non-crystalline materials. Considering the workability and patterning in terms of minimum viscosity, η_{min} concept, the lower η_{min} is preferred. The analytical formability measurements together with the observed thermal stability and viscosity data suggest that the $Gd_{60}Cu_{25}Al_{15}$ and $Gd_{60}Cu_{25}Al_{13}B_2$ metallic glasses are the most advantageous to patterning among the prepared Gd-based MGs in the present research, owing to their higher thermal stability and lower viscosity at the supercooled liquid state besides to their large ability to interact with neutron supported by the Gd constituent **(Chapter 3)**.

The main objective of this work is to fabricate thick, large area grating with pitch of several micrometers; therefore, the next approach is to find the optimum condition for imprinting and prepare the high aspect ratio grating made of Gd-based alloys. The imprinting experiments were performed at two different conditions; namely, isothermal in SCLR and isochronal above T_x to reach the best condition for imprinting. At isothermal condition the samples were heated to several temperatures at the SCLR for about several periods (to maintain glassy structure after the process, isothermal imprinting should be finished within the incubation time (τ) for the crystallization which is investigated by isothermal DSC measurement) and meanwhile they were under stress. The imprinting experiments at isothermal conditions were not successful and the maximum filling depth was only ~4 µm, which is just ~1/4 of the required value. In fact, a good diffraction grating needs to be at least with 10 µm heights even for 100% Gd metal in case for neutron imaging at a neutron wavelength of 4 Å, thus, grating with these Gd-based alloy gratings with less Gd concentration ~60at% is required to have at least 10/0.6= 16 µm height. Therefore, the results of isothermal imprinting were not satisfied. This is because of the fact that Gd-based metallic glasses are less fragile and thus strong as well as they show low thermal stability. The reason to do isothermal imprinting was to keep the glassy structure even after imprinting; however, this method was found to be unsuccessful, so the condition for imprinting needs to be changed. The alternative method to do imprinting is isochronal imprinting. In this method the crystallization of the sample during the experiments is acceptable as the neutron imaging affected only by the Gd constituents of the gratings not by the structure or strength of the gratings. At isochronal imprinting the samples were heated up to the offset temperature of the crystallization at higher heating rate and at the same time they were pressed into the Si mold. According to the TMA analysis, the flow continues even after the temperature reaches the onset temperature of the crystallization and that is why we did the imprinting at the offset crystallization temperature. In summary, the logic why the isochronal imprinting might be successful compared with the isothermal imprinting is as a result of the fact that the imprinting experiments are done at the maximum temperature in which the flow is possible; in this framework the maximum filling depth can be derived. The SEM images of the section of the gratings fabricated at the isochronal conditions show that the 9 µm pitch and ~30 µm heights grating can be faithfully fabricated using $Gd_{60}Cu_{25}Al_{15}$ and $Gd_{60}Cu_{25}Al_{13}B_2$ alloys, by allowing crystallization during a rapid heating isochronal imprinting process at a heating rate of 10 K/s and under the stress of 100 MPa. Furthermore, heating rate and applied stress dependence on the experimental filling depth; in other words, grating thickness show that increasing heating rate as well as stress leads to increase of the thickness of the gratings. These data are fitted well by the data calculated based on the Hagen-Poiseuille equation for $Gd_{60}Cu_{25}Al_{15}$ grating alloys **(Chapter 4)**.

The neutron grating interferometer setup was established at the Energy-Resolved Neutron Imaging System, RADEN, which is installed at beam line BL22 of the J-PARC Materials and Life Science Experimental Facility (MLF). The beam power was 500 kW. Neutrons with a center wavelength of 5 Å and a wavelength distribution $\Delta\lambda/\lambda$ of 18% were chosen. The experimental setup consists of three gratings; namely, source grating G0 made of Gd_2O_3, phase grating G1 made of Si and analyzer grating G2 made of Gd-based alloys. The source grating was placed at a distance of 17,235 mm from the neutron source to provide spatial coherence for the interference experiment. The phase grating induces a $\frac{\pi}{2}$ phase shift and it was placed at a distance of 1,539 mm from source grating. The analyzer grating was located at the distance of 77 mm to the phase grating. In the setup the source size was defined by a circular aperture with a 50.1 mm in diameter located at 3,100 mm from the source and the illumination area was limited to 60 $\times$ 60 mm^2 using a B_4C slit placed in front of the source grating. A neutron image detector composed of an EMCCD camera with an effective pixel size of 31.6 µm and 1,004 $\times$ 1,002 pixels and a 100 µm thick $ZnSLi_6F$ scintillator was used. The spatial resolution was 190 µm. The grating used in the present neutron grating interferometry setup was made of $Gd_{60}Cu_{25}Al_{15}$ and the height of the grating was estimated to be ~26 µm. The performance of the grating interferometry was experimentally tested by pixel wise evaluating the visibility over the grating area and it was concluded that the visibility was homogenously distributed over the grating area with an average value of 61%. The visibility contains information about the maximum contrast of the grating interferometer setup. This value for visibility of the neutron grating interferometry is much higher than the visibility of other kinds of gratings reported to date. The higher visibility is due to the fact that neutrons are more efficiently absorbed by the high aspect ratio new grating made of $Gd_{60}Cu_{25}Al_{15}$. Moreover, transmission and differential phase shift contrast imaging were obtained successfully for aluminum and vanadium rod samples **(Chapter 5)**.

This is the first report of successful imprinting of Gd-based MG with less viscous workability and it can creates a paradigm for future studies of patterning even less viscous workable MG. Furthermore, the novel high aspect ratio is expected to be a breakthrough for neutron imaging in material science and industry applications; for instance, to show high contrast image of an object in neutron radiography/tomography applications.